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On the release of volatile acids from wood-based panels – chemical aspects –

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Abstract Wood-based panels release different amounts of volatile organic acids, which depend, among other factors, on the binder used. The volatile acids released from the boards can be measured using the flask method following the principle of measuring the formaldehyde release according to EN 717-3. Particleboards bonded with alkaline curing phenol-formaldehyde resins (PF-boards) release higher amounts of acetic and lower amounts of formic acid compared to those boards bonded by acid curing urea-formaldehyde reins (UF-resins) or binders based on polymeric diphenylemethandiisocyanates (PMDI). This has been explained by the equilibrium reaction between sodium hydroxide in PF-resins and volatile acids, which leaves less free formic acid than free acetic acid to emanate from the boards. Increasing the binder content in the boards also leads to an increase in the over all amount of sodium hydroxide in the boards. Accordingly, less free acids are left, which could be released from the boards. Fibres made by the chemo-thermo-mechanical process (CTMP) using sodium hydroxide and sodium sulphite as pulping agents release less formic acid than those made by the thermo-mechanical pulping (TMP). This behaviour was also attributed to the equilibrium reaction between the alkali in CTMP-boards and the volatile acids.

Über die Abgabe von flüchtigen Säuren aus Holzwerkstoffen – chemische Aspekte –

Zusammenfassung Holzwerkstoffe geben u. a. in Abhängigkeit von dem verwendeten Bindemittel unterschiedliche Mengen an Ameisen- und Essigsäure ab, die nach dem Prinzip der Flaschenmethode in Anlehnung an die Vorgehensweise bei der Bestimmung der Formaldehydabgabe nach EN 717-3 bestimmt werden können. Mit alkalisch härtenden Phenolformaldehydharzen hergestellte Holzspanplatten (PF-Platten) geben weitaus mehr Essigsäure und viel weniger Ameisensäure ab als jene die mit Säure härtenden Harnstoffformaldehydharzen (UF-Harze) oder mit Klebstoffen auf Basis von polymeren Diphenylmethandiisocyanaten (PMDI) hergestellt wurden. Dies wird damit erklärt, dass es zwischen dem Alkali in PF-Spanplatten und den flüchtigen Säuren zu Gleichgewichtsreaktionen kommt, bei denen mehr Formiationen als Acetationen im Gleichgewicht sind. Eine Erhöhung des Bindemittelanteils in PF-Spanplatten verringert die Abgabe von Essig- und Ameisensäure, da hierdurch zwangsläufig die Alkalimenge in den Platten erhöht wird, die die Bildung von Formiat- und Acetationen forciert. Auch aus den Fasern, die nach dem chemo-thermo-mechanischen Prozess (CTMP) hergestellt wurden, entweicht mehr Essigsäure und weniger Ameisensäure als aus den Fasern, die nach dem thermo-mechanischen Prozess (TMP) hergestellt sind. Dies wird auch durch die Gleichgewichtsreaktion zwischen dem Alkali und den flüchtigen Säuren erklärt.

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1 Introduction

Wood has usually a slightly acidic pH-reaction with water (Stamm 1961). Moreover, wood releases, even under ambient conditions, different amounts of volatile organic acids, like acetic and formic acid (Packman 1960, Sandermann et al. 1970). The amount and the chemical composition of volatile acids liberated from wood can change tremendously in the course of different processes like drying, steaming and pulping. In such processes the main wood components (cellulose, hemicelluloses and lignin) and also their extractives are more or less involved. A veritable spate of publications covers this subject (Enger 1951, Jayme and Reimann 1958, Roffael 1987, Risholm-Sundman et al. 1998).

Industrial production of wood-based panels like particle- and fibreboards include steps like drying (particleboard), steaming and thermohydrolysis (fibreboard), which promote the formation of volatile organic acids from wood. Moreover, volatile organic acids can be generated during board manufacture through interaction between the binder and wood. Alkali (sodium hydroxide), e.g. in phenol formaldehyde resins, deacetylates wood leading to the formation of sodium acetate and, therefore, to the liberation of acetic acid (Klauditz 1957, Roffael et al. 1990). Moreover, the reaction between sodium hydroxide and formaldehyde during resin manufacture and in PF-bonded boards leads to the formation of formic acid via sodium formate (Cannizzaro reaction). In UF-resins there is always some formic acid included. Insofar, the release of volatile acids from wood-based panels is a complex function of different factors. However, it seems that almost no systematic research work has been carried out on the emission of volatile organic acids from wood-based panels till the late eighties of the last century.

2 Results and discussion

In 1988, the emission of volatile organic acids from particle- and fibreboards was studied using the flask method, originally developed to assess the formaldehyde release from wood-based panels (EN 717-3 1996). The formaldehyde and the volatile acids released from the boards are determined as a function of the reaction time. The measurement of volatile acids is conducted by ion chromatography.

Using this technique, the release of volatile organic acids from differently bonded particle boards at different temperatures was assessed (Roffael 1988). The results showed that particleboards bonded with alkaline phenolic resins (PF-resins) generally emit higher amounts of acetic acid than particleboards made by using acid curing urea formaldehyde resins (UF-resins) or binders based on polymeric isocyanates (PMDI). In-depth research work showed that the acetyl groups in wood hemicelluloses are degraded under the alkaline conditions used in making PF-boards. Moreover, the results indicate surprisingly that the release of formic acid from PF-bonded particleboards is very low compared to that from UF-bonded or PMDI-bonded particleboards. At 20 °C, the release of formic acid from PF-boards was not even detectable, whereas, e.g. PMDI-bonded boards still release relatively high amounts of formic acid (Figs. 1 and 2).

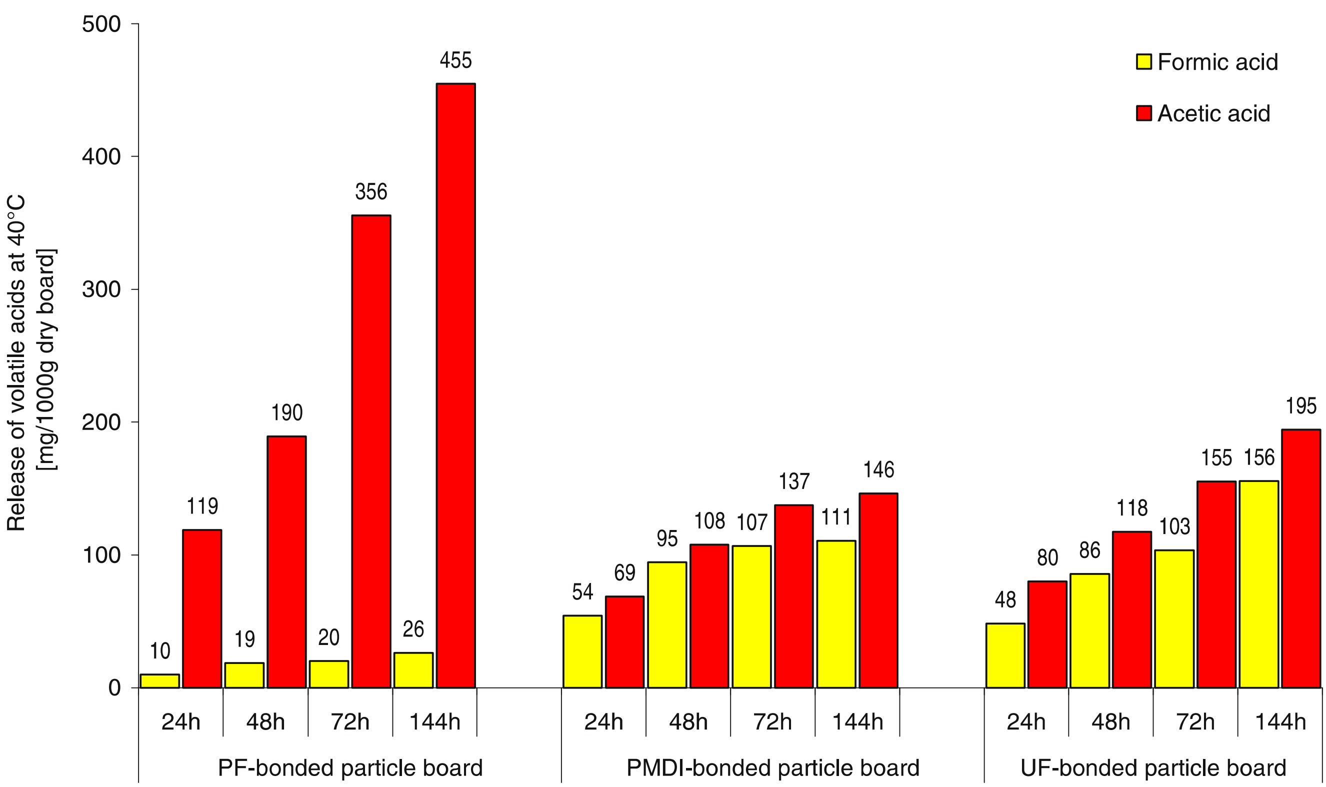

Fig. 1 Release of volatile organic acids from PF-, PMDI- and UF-bonded particleboards at 40 °C
Abb. 1 Abgabe von flüchtigen Säuren aus PF-, PMDI- und UF-gebundenen Holzspanplatten bei 40 °C

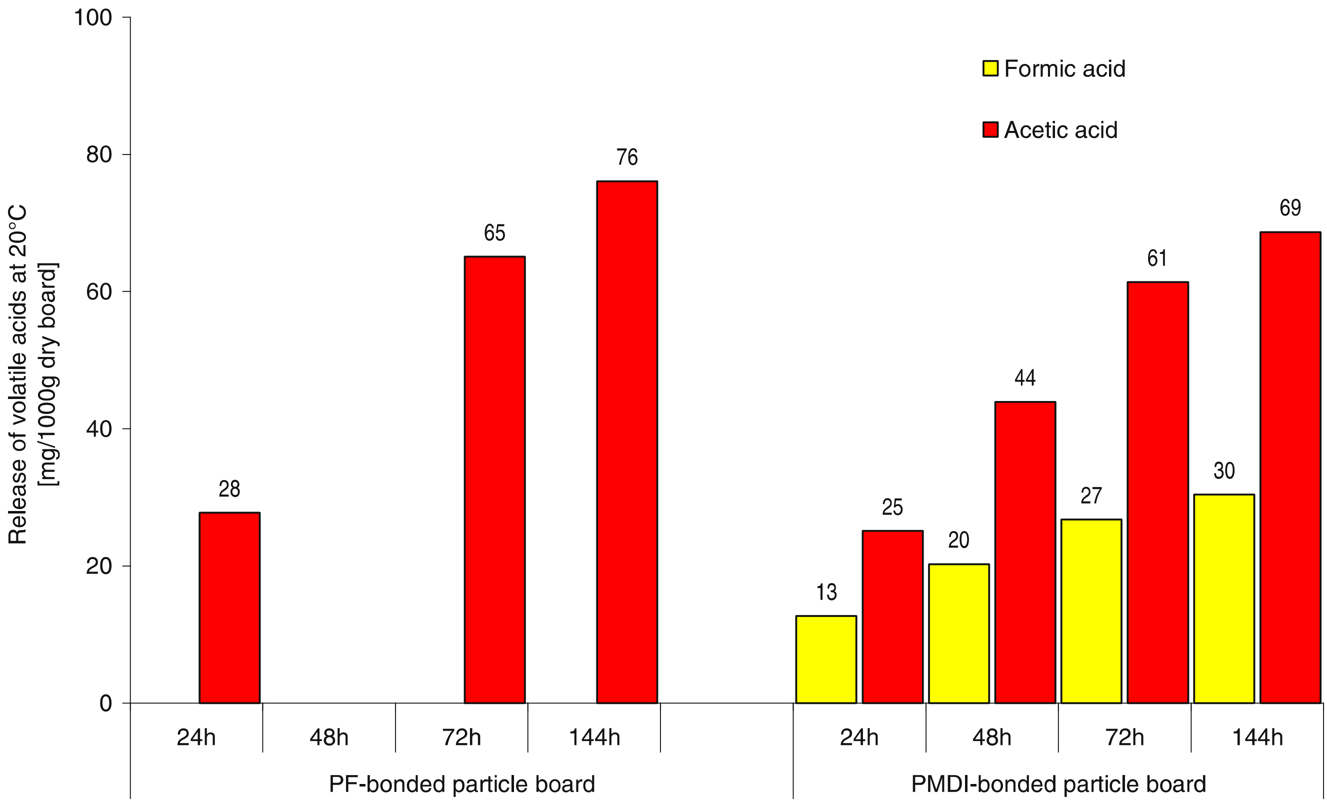

Fig. 2 Release of volatile organic acids from PF- and PMDI-bonded particleboards at 20 °C. The emission of formic acid from PF-boards is not detectable

Abb. 2 Abgabe von flüchtigen Säuren aus PF- und PMDI-gebundenen Holzspanplatten bei 20 °C

This phenomenon can be explained as follows: Sodium hydroxide in PF-resins reacts with formic and acetic acid leading to the formation of sodium formate and sodium acetate, respectively. As formic acid is a much stronger acid compared to acetic acid, formic acid will be first buffered by sodium hydroxide and then acetic acid. Accordingly, the release of formic acid will be more strongly suppressed by the presence of sodium hydroxide than that of acetic acid. Insofar, the release of volatile acids from PF-boards seems to be controlled by the chemical equilibrium resulting from the reaction between sodium hydroxide and the volatile acids (Fig. 3).

In further research work, boards were made from pine heartwood and pine sapwood using two different resin levels (8.5 and 14%). The amount of acids released using the flask method as well as the formate and acetate ions in the cold water extracts were measured. The results are shown in Figs. 4 and 5.

The results reveal that increasing the resin level from 8.5 to 14% decreases the release of both acetic acid and formic acid. As the increase in the resin level is accompanied at the same time by an increase in the alkali level, which buffers up the acids in the particle- and fibreboards leading to the formation of sodium acetate and sodium formate and increases the pH-value of the boards, it is understandable that the release of acids declines to lower values due to the shift of the equilibrium to the right hand side of the equation. The decrease occurs though the amount of formate and acetate ions in the cold water extracts increased by the higher amount of alkali (Figs. 4 and 5). No significant differences were found in the release of acids from PF-boards made from sap- and heartwood.

The above mentioned results are in line with the work published recently by Roffael et al. (2007) on the emission of acids from chemo-thermo-mechanical (CTMP) and thermo-mechanical pulps (TMP) and from boards prepared thereof. The results show that the CTMP-process, which uses sodium hydroxide and sodium sulphite as a pulping

$$\mathrm{H{\cdot}COOH + NaOH \rightleftarrows H{\cdot}COO^{-}Na^{+} + H_2O} \quad (\mathrm{pKa} = 3.7)$$

$$\mathrm{CH_3{\cdot}COOH + NaOH \rightleftarrows CH_3{\cdot}COO^{-}Na^{+} + H_2O} \quad (\mathrm{pKa} = 4.8)$$

Fig. 3 Reaction between volatile acids (formic and acetic acid) and sodium hydroxide

Abb. 3 Reaktionen zwischen flüchtigen Säuren (Ameisen- und Essigsäure) und Natriumhydroxid

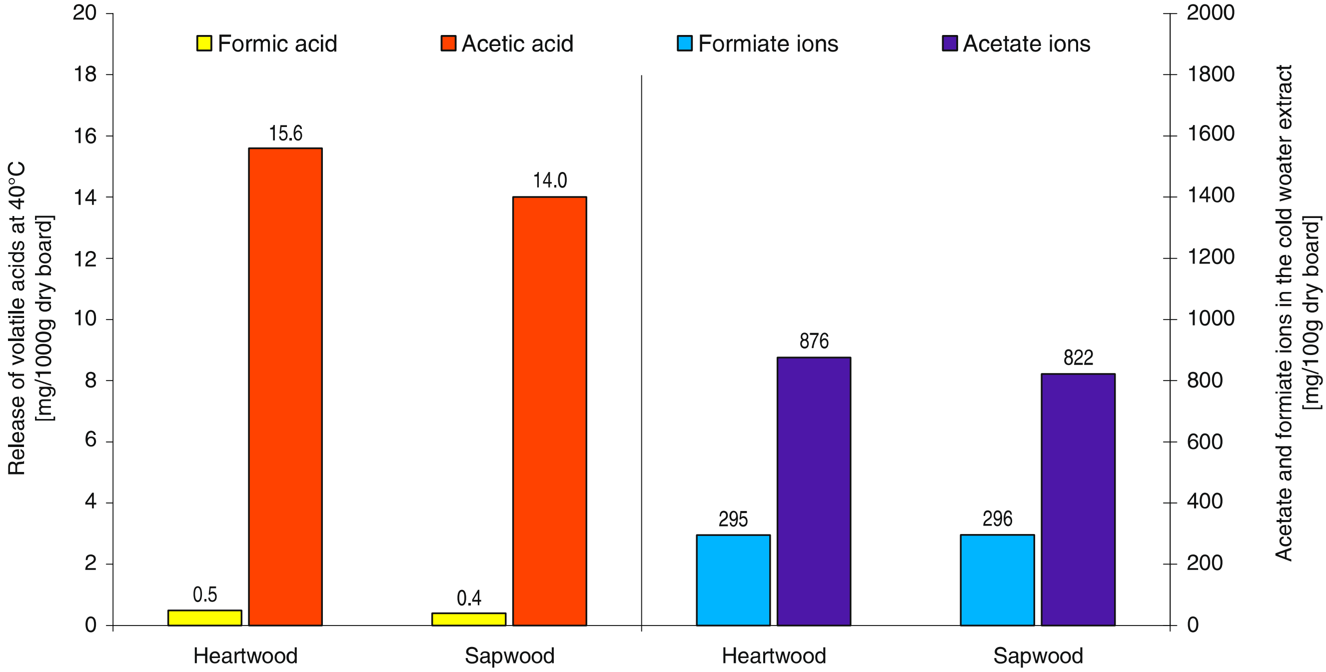

Fig. 4 Release of volatile organic acids from PF-bonded particleboards made from heart- and sapwood of pine at a binder level of 8.5%, the contents of formate and acetate ions in cold water extracts are also presented. Alkali content of the used PF-resin was nearly 17% (based on solids)

Abb. 4 Abgabe von flüchtigen Säuren aus PF-gebundenen Holzspanplatten (Bindemittelanteil 8,5%), hergestellt aus Kern- und Splintholz der Kiefer (Pinus sylvestris). Der Gehalt an Formiat- und Acetationen in den Kaltwasserextrakten ist mit aufgeführt. Der Alkaligehalt des Bindemittels ist etwa 17% (bezogen auf Feststoff)

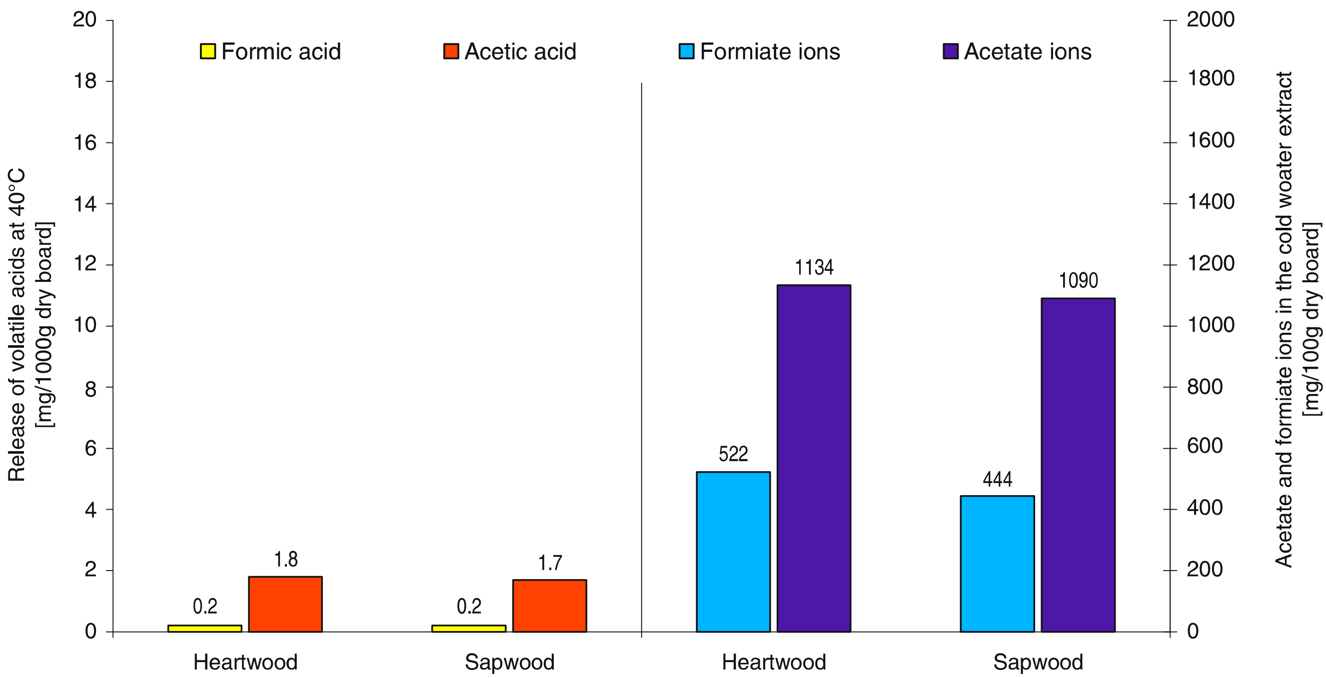

Fig. 5 Release of volatile organic acids from PF-bonded particleboards made from heart- and sapwood of pine at a binder level of 14%, the contents of formate and acetate ions in cold water extracts are also presented. Alkali content of the used PF-resin was nearly 17% (based on solids)

Abb. 5 Abgabe von flüchtigen Säuren aus PF-gebundenen Holzspanplatten (Bindemittelanteil 14%), hergestellt aus Kern- und Splintholz der Kiefer (Pinus sylvestris). Der Gehalt an Formiat- und Acetationen in den Kaltwasserextrakten ist mit aufgeführt. Der Alkaligehalt des Bindemittels ist etwa 17% (bezogen auf Feststoff)

Fig. 6 Chemical properties of thermo-mechanical (TMP) and chemo-thermo-mechanical pulps (CTMP) derived from Scots pine (Pinus sylvestris [L.])
Abb. 6 Chemische Eigenschaften von thermo-mechanischen (TMP) und chemo-thermo-mechanischen (CTMP) Holzfaserstoffen, hergestellt aus Kiefernholz (Pinus sylvestris [L.])

Properties	Pulping method and pulping conditions*	
	TMP	CTMP 0.5 % NaOH 1 % Na_2SO_3
Content of cold water extractives (% o.d. fibres)	4.4	4.6
Content of hot water extractives (% o.d. fibres)	5.4	5.7
pH-value	4.5	5.5
Buffering capacity (mmol NaOH/ 100g o.d. fibres)	1.50	1.61
Content of formates and acetates in cold water extractives (mg/ 100g o.d. fibres)		
Formates	**8.0**	**89.8**
Acetates	**44.1**	**288.7**
Release of volatile acids [flask method] (mg/ 100g oven dried fibres)		
Formic acid	**2.4**	**1.7**
Acetic acid	**4.3**	**38.3**
Formaldehyde release [flask method] (mg/ 1000g oven dried fibres)		
3 h	2.3	2.0
24 h	33.3	14.5

* Pulping conditions: 170 °C, 5 min

Fig. 7 Chemical properties of binderless fibreboards made from thermo-mechanical and chemo-thermo-mechanical pulps derived from Scots pine (Pinus sylvestris [L.])
Abb. 7 Chemische Eigenschaften von bindemittelfreien Holzfaserplatten, hergestellt aus thermo-mechanischen (TMP) und chemo-thermo-mechanischen (CTMP) Faserstoffen aus Kiefernholz (Pinus sylvestris [L.])

Board properties	Pulping method and pulping conditions*	
	TMP	CTMP 0.5 % NaOH 1 % Na_2SO_3
	binderless	binderless
Moisture content (%)	6.3	6.7
Extractive content (cold water) (% o.d. board)	6.3	5.8
Extractive content (hot water) (% o.d. board)	6.6	6.3
pH-value	4.6	5.7
Buffering capacity (mmol NaOH/ 100g o.d. board)	1.58	1.07
Content of formates and acetates in cold water extractives (mg/100g o.d. board)		
Formates	**1.8**	**79.4**
Acetates	**46.1**	**175.5**
Release of volatile acids [flask method] (mg/100g oven dried board)		
Formic acid	**2.0**	**1.5**
Acetic acid	**8.8**	**38.9**
Formaldehyde release [flask method] (mg/1000g oven dried board)		
3 h	8.8	1.8
24 h	58.1	10.5

* Pulping conditions: 170°C, 5 min

agent, deacetylates wood and enhances therefore the formation of acetate ions in the fibres and the boards prepared therefrom. However, the release of formic acid was less than that from thermo-mechanical pulps. On the other hand, the liberation of acetic acid is enhanced by the CTMP-process (Figs. 6 and 7). The CTMP-process also decreases the formaldehyde release of the fibres (Fig. 6) and of the boards prepared thereof (Fig. 7).

3 Conclusion

The whole results lead to the following conclusions:

1. Release of volatile organic acids from wood and wood-based panels can be assessed using the flask-technique originally developed for measuring the formaldehyde release of boards.

2. In particle- and fibreboards interaction between the resin and wood has a decisive influence on the release of volatile acids from the boards.
3. PF-boards emit higher amounts of acetic acid compared to PMDI- and UF-boards. However, the emission of formic acid is significantly lower.
4. In PF-bonded boards the release of volatile acids seems to be controlled by equilibrium resulting from the reaction between sodium hydroxide and the liberated acids.
5. The release of volatile acids could decrease by increasing the alkali content in PF-bonded boards due to shift in the equilibrium reaction.

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